U.S. Department of Energy

Livermore Site Office, Livermore, California 94551

Lawrence Livermore National Laboratory

Lawrence Livermore National Security, LLC, Livermore, California 94551

LLNL-AR-412616

Resolution of Mixed Waste Management Issues Associated with Operation of Soil Vapor and Ground Water Treatment Facilities at LLNL, Livermore Site

April 30, 2009

Environmental Restoration Department

This work performed under the auspices of the U. S. Department of Energy by Livermore National Laboratory under Contract DE-AC52-07NA27344.

LLNL-AR-412616

Resolution of Mixed Waste Management Issues Associated with Operation of Soil Vapor and Ground Water Treatment Facilities at LLNL, Livermore Site

April 30, 2009

Resolution of Mixed Waste Management Issues Associated with Operation of Soil Vapor and Ground Water Treatment Facilities at LLNL, Livermore Site

This paper discusses issues related to operation of soil vapor and ground water treatment facilities at the LLNL Livermore Site that generate mixed waste granular activated carbon (GAC) and summarizes actions taken to resolve these issues. Three of these facilities are located in the Trailer 5475 area (TF5475-1, TF5475-3, and VTF5475) (Figure 1) and one facility is near Building 518 (TF518 North) (Figure 2).

Sources of Mixed Waste

GAC is widely used to remove volatile organic compounds (VOCs) from contaminated ground water and soil vapor by treatment facilities at the LLNL, Livermore Site. The majority of the LLNL GAC canisters are used in areas not impacted by tritium and become spent with VOCs that have been removed from the ground water or soil vapor. This spent GAC is sent to an off-site vendor for recycling. The TF5475-1, TF5475-3, VTF5475 and TF518-N facilities have been impacted by tritium in the form of tritiated water (HTO) and have a common problem of mixed-waste generation (e.g., GAC containing tritium and VOCs). However, each facility is somewhat unique in its operational history that may influence how to successfully treat contamination while minimizing waste stream management costs. The history of each of the treatment facilities is briefly described below.

Trailer 5475 treatment units

Remedial Design Report No. 4 for Trailer 5475 Treatment Facilities (Berg et al., 1998) evaluated and proposed remedies for treating VOCs beneath the Trailer 5475 (T5475) area using catalytic reductive dehalogenation (CRD) technology and GAC. The treated ground water or soil vapor containing tritium would then be re-injected into the subsurface where the tritium would decay naturally.

Treatment Facility 5475-1 (TF5475-1) - The initial groundwater treatment system was designed to treat VOCs in ground water *in situ* in a well completed in Hydrostratigraphic unit (HSU) 3A by utilizing a catalytic reductive dehalogenation process with dissolved hydrogen in the presence of a palladium catalyst. This led to the design and installation of CRD1 in September 1998. While this unit was effective in treating VOCs, it became apparent over time that it was more difficult to consistently meet the 90% destruction efficiency of recalcitrant VOCs. As discussed in the June 10, 2005 Remedial Project Manager (RPM) meeting minutes, liquid aqueous phase carbon (i.e., GAC) was to be added after CRD1 treatment to mitigate this issue. The GAC became operational in

August 2005 and successfully removed residual VOCs from the treatment stream (Berg and Wong, 2005a and 2005b). This facility has been shut down since July 26, 2007.

Vapor Treatment Facility 5475 (VTF5475) - Contaminated soil vapor from HSUs 2 and 3A was proposed to be treated in a closed loop system in which soil vapor containing VOCs and tritium was extracted from the subsurface, the VOCs removed from the vapor stream using GAC, and then vapor containing tritium was re-injected back into the subsurface to decay naturally. It was proposed that by managing the temperature and humidity of the extracted soil vapor, the tritium would remain in the vapor phase, pass through the treatment system and be re-injected into the subsurface. The GAC would periodically be replaced and the spent GAC sent to LLNL's waste management organization to arrange off-site regeneration or disposal of the GAC, as appropriate. VTF5475 was built and began operating in January 1999. The soil vapor extraction well network was later expanded and the treatment system modified in support of ERD's enhanced source area remediation initiative. This facility was shut down October 12, 2007.

Treatment Facility 5475-3 (T5475-3) - Because of hydrogeologic and treatment system design limitations, an Explanation of Significant Differences for Trailer 5475 Ground Water Remediation (Berg, 2000) was prepared in February 2000, to present a proposal to treat VOCs in a larger, above-ground CRD unit and re-inject the treated ground water containing tritium back into the subsurface. The alternate design was approved, constructed and began operating in September 2000. An additional extraction well was added to this facility, rather than building a new CRD unit to meet the September 2006 TF5475 South milestone. This facility treats ground water from HSUs 3A, 4 and 5. As operation of this facility progressed, a number of technical challenges were encountered, requiring constant monitoring, maintenance and adjustments in order to avoid treatment facility upsets. A number of these issues are documented in RPM meeting minutes. Ion–exchange canisters were added to treat for excess chromium in early 2006. To help ensure that VOCs were adequately removed prior to reinjection of treated ground water into the subsurface, GAC was also added to the treatment train in June 2006. (Berg and Wong, November 2005 and February 2006) This facility has been shut down since August 21, 2007.

Treatment Facility 518 North (TF518-N)

TF518-N was designed to treat VOC-contaminated ground water from HSU 4 by running it through a GAC canister. No tritium was present in this area when the facility was designed and became operational in January 2000. However in 2007, anomalous tritium activities were detected in a treatment system influent sample and as a result, the spent GAC required management as a mixed waste. This facility has been shut down since February 20, 2008.

Waste Management at LLNL

At LLNL, the Radioactive and Hazardous Waste Management (RHWM) Division has the primary responsibility of accepting and managing hazardous, radioactive, and mixed waste from LLNL generators such as ERD. RHWM operates permitted storage and treatment facilities on-site, and RHWM also arranges shipment to off-site vendors for further treatment and disposal at appropriately permitted treatment, storage and disposal facilities (TSDFs). Limited on-site treatment capabilities and few off-site disposal options make the disposal of mixed wastes difficult and very expensive. Thus, LLNL generators are expected to take all possible efforts to minimize mixed-waste generation and to reduce the volume or quantity and toxicity of hazardous waste to the degree determined to be economically practical (ES&H Manual, Document 30.1, 2009).

Mixed waste is waste that contains both radioactive and hazardous components as defined by the Atomic Energy Act (AEA) and the Resource Conservation and Recovery Act (RCRA), respectively. Mixed waste generated at LLNL is managed in accordance with DOE Order 435.1 and DOE M 435.1-1, as well as the requirements of RCRA and the AEA. The Federal Facilities Compliance Act (FFCA) also defines mixed waste as waste that contains hazardous waste and source, special nuclear, or byproduct material subject to the AEA of 1954. The FFCA further requires DOE facilities that generate mixed waste to submit to the EPA mixed waste inventory, national treatment capacity and technology inventory and plans for developing treatment capacities and technologies for mixed waste. For LLNL, DOE meets these requirements via its the Livermore Site Office, NNSA.

Based on very limited experience with arranging off-site treatment and disposal of legacy mixed wastes, RHWM staff estimated in 2006 that it would cost approximately $16,000 per 55-gallon drum to send the mixed waste GAC to an appropriately permitted TSDF.

What Has Been Done to Solve Mixed Waste GAC Issues?

Several questions were asked in the process of evaluating whether more cost-effective options were available to manage waste generated by the 4 facilities described above. These questions included:

1. Is the waste appropriately characterized?
2. Are there regulatory processes that would allow access to a wider suite of off-site treatment and disposal facilities?
3. Are there operational parameters that could be modified to minimize or eliminate the amount of mixed waste generated?
4. Are there other technologies available to treat the soil vapor or ground water without generating mixed waste?

Actions taken to respond to these questions are discussed in more detail below.

Is the waste appropriately characterized?

LLNL's Environmental Restoration Department (ERD) had previously taken a very conservative approach in characterizing waste and declared VOC-contaminated ground water in the area of Trailer 5475 to be F-listed waste, as it was believed the contamination resulted from degreasing operations that occurred when the Livermore Site was used as a Navy air training base. RHWM reviewed the documentation on how waste was generated, prior interpretations of how to apply hazardous waste characterization criteria, and current applicable regulations and regulatory guidance. Based on this review, it was determined that wastes resulting from cleanup activities could be characterized as hazardous due to toxicity (D-coded) and that it is not possible to assign any of the F001-F005 codes to LLNL remediation waste because the specific sources of contaminants cannot be definitively determined.

RHWM has sampled the current inventory of stored waste to plan and negotiate the ultimate disposition. Of the 35 drums currently in storage, 23 drums proved to contain constituents in excess of hazardous waste thresholds and must continue to be managed as mixed waste. The remaining 12 were below the hazardous waste thresholds and will be managed as radioactive low-level waste. RHWM is in negotiation with two off-site vendors who have the appropriate, permitted treatment and disposal capabilities to accept both the low-level radioactive and the mixed waste GAC waste. Once all the appropriate reviews and approvals are completed, and necessary contractual documentation is in place, the existing backlog of mixed waste will be sent to the selected vendor's TSDF for treatment and final disposal. This is expected to occur this fiscal year.

Also as a result of this change in approach to characterization, ERD has the opportunity to review and adjust operational parameters that may keep the GAC from becoming hazardous due to toxicity (e.g., more frequent change out of GAC) based on sampling and analysis of waste streams. However, this approach needs further evaluation, as this would potentially generate more waste, albeit less problematic to manage, contrary to principles of waste minimization and pollution prevention.

In addition to the hazardous characteristic, the spent GAC needed to be evaluated against DOE's requirements for managing radioactive waste due to the presence of tritium. When the treatment system was first designed for treating the VOC and tritium contaminated vapor at VTF5475, it was believed that tritium would preferentially stay in the vapor stream in the vapor extraction system rather than absorb to the carbon and then be re-injected into the subsurface. Operational experience showed that some water was retained in the GAC canisters containing measurable quantities of tritium. Therefore, radioactive waste management requirements were applicable.

DOE Moratorium on Radioactive Waste

DOE placed a moratorium on the shipment of potentially contaminated waste circa 1991 until each site could develop a set of procedures and/or processes to determine if the waste to be shipped off site contained radioactivity added by that sites' activities. The set of documents that described the processes to be used at LLNL are generically known as the moratorium document. LLNL's moratorium document was reviewed and approved for use by DOE in 1992.

This moratorium describes when waste should be managed as material containing residual radioactivity or managed as non-radioactive. The underlying purpose was to ensure that wastes generated from activities sponsored by the DOE are properly managed. Waste with residual radioactivity is managed as "rad-added" and may only be sent to DOE authorized facilities for disposal.

LLNL relies on trained waste generators as the first step in determining the nature of the waste they generate. Generators must certify the nature of their waste before RHWM will accept it for storage, treatment, and/or disposal. If the generator is uncertain about the level of hazardous and/or radioactive materials in the waste, the material is sampled and analyzed at an approved analytical laboratory. The analytical results are evaluated to determine the appropriate waste type.

The following table lists the maximum Minimum Detectable Concentration (MDC) values analytical laboratories can use when analyzing different waste matrices for radioactivity.

Table 1: MDC Values by Matrix

Matrix	Gross alpha	Gross Beta	Tritium
Aqueous (Retention tanks, Berms, Rain water)	20 pCi/L	60 pCi/L	3000 pCi/L
Aqueous (Spent chemicals, mop water, coolants)	1500 pCi/L	2000 pCi/L	3000 pCi/L
Oil	5000 pCi/L	10,000 pCi/L	40,000 pCi/L
Solids, sludges	6 pCi/gm	10 pCi/gm	5 pCi/gm
Solvents	1500 pCi/L	2000 pCi/L	40,000 pCi/L

For purposes of characterizing the spent GAC from ERD's treatment facilities, the GAC falls within the "solids, sludges" matrix. Therefore any analytical results at or above 5 pCi/gm tritium would indicate the waste has "rad-added" and would need to be managed as low-level radioactive waste. Sample analyses of the spent GAC demonstrate

that tritium activities are low but still above the MDC value of 5 pCi/gm (majority of samples less than 50 pCi/gm with a maximum of 160 pCi/gm).

Are there regulatory processes that would allow access to a wider suite of off-site treatment and disposal facilities?

As previously discussed, the spent GAC must be managed to comply with both RCRA regulations for hazardous waste and DOE requirements for managing radioactive waste under DOE Order 435.1. The ability to characterize the waste as D-coded versus F-listed waste has opened some opportunities for demonstrating whether waste must be managed as hazardous waste. However approximately two-thirds of the waste stream that has already been generated is still considered mixed waste and there is the potential for creating additional mixed waste in the future. The DOE Manual (DOE M 435.1-1) that provides more detailed requirements to implement DOE Order 435.1 and regulating radioactive waste contains a provision for "Release of Waste Containing Residual Radioactive Material" that LLNL has pursued. DOE M 435.1-1 defines this provision as "Processes for determining and documenting that waste is suitable to be released and managed without regard to its radioactive content shall be in accordance with the criteria and requirements in DOE 5400.5, *Radiation Protection of the Public and the Environment*" also known as 'Authorized Limits'.

In mid 2006, LLNL issued a task order to a subcontractor, Weiss Associates, to prepare a risk evaluation to support an Authorized Limits petition for RHWM to use in negotiating off-site treatment and disposal.

As defined in DOE Order 5400.5, an Authorized Limit is a level of residual radioactive material that will result in an annual public dose of 100 milliroentgen-equivalent man per year (mrem/year) or less. In 1995, DOE issued additional release requirements for material sent to a landfill that is not an authorized low-level radioactive waste disposal facility. Per guidance, the disposal site will be selected based on a risk/benefit assessment under the As-Low-As-Reasonably-Achievable (ALARA) process while ensuring that individual doses to the public are less than 25 mrem in a year, ground water is protected, the release would not necessitate further remedial action for the disposal site, and the release is coordinated with all appropriate authorities. The 1995 release requirements also state that Authorized Limits may be approved by DOE field office managers without DOE headquarters' (EH-1) approval if a reasonably conservative dose assessment demonstrates that:

- Public doses will not exceed 1 mrem per year individually or 10 person-rem/year collectively;
- Appropriate record keeping and data collection procedures are in place;
- Copies of the release evaluation and procedures are properly maintained;
- Coordination with all applicable state and federal agencies is documented.

Weiss Associates conducted its evaluation according to the Authorized Limit procedures specified in DOE Order 5400.5, *Radiation Protection of the Public and the Environment (DOE, 1993)* and related DOE guidance documents. Based on the above guidelines, the Weiss report used a *de minimus* public dose limit of 1 mrem/year for individual members of the public and 10 person-rem/year for the collective population.

A draft report dated January 9, 2007 was prepared and transmitted to LLNL for use in negotiations that outlined the process used to evaluate the potential impact on a specified permitted TSDF. (Weiss, January 2007). As a result, Authorized Limits of 4,400 pCi/gm for tritium, and 1,100 pCi/gm for lead-210, bismuth-210 and polonium-210 were proposed. Since the evaluation requires detailed modeling of impacts from shipment to final disposition, the proposed limits are site specific, and in this case were based on sending this waste stream from LLNL to a facility in Texas. As stated in the report, these limits result in a maximum dose of approximately 0.01 mrem/yr to a member of the public. Disposal of the waste GAC at the specified facility would be a restricted release under DOE Order 5400.5 and must conform to the assumptions and exposures scenarios used in this report, as such, the GAC must be:

- Composed of granular carbon not previously used for remediation or filtering purposes.
- Treated and disposed at the specified facility (or any future operator) in Texas provided it continues to handle, process and dispose the GAC waste in a manner consistent with the current practices and permit requirements at they are currently understood and documented in this report.
- Stored for a minimum of 24-hours after being removed from the vapor phase treatment train to allow short-lived radon daughter products to decay.
- Shipped for disposal in amounts no greater than one 30-drum shipment in a twelve month period.

Although, the radioactive constituents within the LLNL GAC waste are well within the proposed Authorized Limits, the TSDF elected not to participate in further negotiations with LLNL as they would have potentially had to modify their regulatory permits to accept this waste stream and treat it in their incinerator. It is likely that the economic cost-benefit analysis of accepting a small waste stream such as the LLNL mixed waste GAC, did not warrant the cost to the TSDF of filing necessary paperwork and seeking regulatory approval to accept this waste stream.

LLNL has considered initiating a similar analysis to approach other TSDFs' and particularly those that may accept similar wastes from other DOE sites under established Authorized Limits. However, given the small quantity of this waste stream and experience to date, other engineered and operational solutions are being considered first before initiating more detailed analyses and negotiations.

Are there operational parameters that could be modified to minimize or eliminate the amount of mixed waste generated?

When the vapor treatment system was initially proposed for the Trailer 5475 area, it was recognized that the tritium in the treatment stream could potentially result in mixed-waste GAC. A treatability test was designed and conducted in November 1996 to test the overall feasibility of the proposed system, including demonstrating whether VOCs could be removed from the process-air stream while passing the tritium on to be re-injected into the subsurface. Analysis of GAC used in that test indicated that about 1 pCi/L of tritium was retained in the GAC (Martins, 1996). While this was a short-term test, test results indicated that by careful conditioning of the soil vapor to minimize condensate, tritium concentrations could be kept low while optimizing retention of the VOCs. Some additional tests were conducted at this facility in 2006, to test whether further variation in temperatures or flow rates would impact treatment efficiency and tritium absorption. Leachate testing of various types of unused commercially available GAC were also conducted to assess whether this material was a source of tritium and other radionuclides. Results of the leachate testing showed that all of the tested GAC was within range of natural soil background values for radioactivity. The engineer in charge of this study took another job before a final report was prepared.

Are there other technologies available to treat the soil vapor or ground water without generating mixed waste?

In late 2007, ERD subcontracted with Terranear PMC, LLC, to evaluate treatment systems at the LLNL Livermore Site, including an evaluation of where mixed waste is generated, and to recommend alternative solutions. A summary of their observations and recommendations is contained in a report entitled "Environmental Restorations Department's Site Treatment Systems Assessment" (Terranear PMC, July 2008). While this was a high-level review, several approaches were recommended for further consideration. These included:

- Managing the operation to limit the amount of VOCs to be below hazardous-waste limits,
- Continuing to seek authorized limits for off-site disposal of the waste,
- Exploring *in situ* treatment technologies such as bio-remediation or chemical oxidation,
- Evaluation of whether all of these systems need to be operated in context of the larger treatment network, and
- Flushing of the spent GAC to remove tritium before disposing of the GAC.

With regards to the last bullet, in March 2007, ERD engineering personnel performed a proof-of-principal treatability test on one 55-gallon GAC canister to test the feasibility of removing tritium from the GAC. Results of this test showed that the tritium could be

removed by flushing 4 to 5 GAC pore volumes of clean water through the canister. While the concept looks promising for separating the VOC and tritium waste into separate waste streams, much more work needs to be done to determine whether this is a viable option.

Conclusion

Due to funding issues in 2008, further efforts to find an engineered solution to the mixed waste issue were temporarily shelved. Focused feasibility studies are planned that will examine in more detail much of the work to date and propose remedies for implementation in the future. LLNL will continue to use available resources to identify the best ways to manage its mixed waste and implement actions that solve the current mixed waste issues in a manner that complies with the dual RCRA/AEA regulatory requirements.

References

Berg, L.L., M.D. Dresen, R.W. Bainer, E.N. Folsom and A.L. Lamarre (Eds) (1998) *Remedial Design Report No. 4 for Trailer 5475 Treatment Facilities*, Lawrence Livermore National Laboratory, Livermore Site, Lawrence Livermore National Laboratory, Livermore California (UCRL-AR-126014).

Berg, L.L., (2000), *Explanation of Significant Differences for the Trailer 5475 Ground Water Remediation* (UCRL-AR-13189).

Berg, L.L. and P. W. Wong, (2005a), *Lawrence Livermore National Laboratory Livermore Site Remedial Project Managers' Meeting Summary – March 25, 2005*, May 27, 2005.

Berg, L.L. and P. W. Wong, (2005b), *Lawrence Livermore National Laboratory Livermore Site Remedial Project Managers' Meeting Summary – June 10, 2005*, August 10, 2005.

Berg, L.L. and P. W. Wong, (2006), *Lawrence Livermore National Laboratory Livermore Site Remedial Project Managers' Meeting Summary – October 12, 2006*, November 8, 2005.

U.S. Department of Energy (DOE) DOE Order 435.1, *Radioactive Waste Management.*

U.S. Department of Energy (DOE) DOE M 435.1-1, *Radioactive Waste Management Manual.*

ES&H Manual, (2009), *Environment, Safety, and Health, Volume III, Part 30: General Environmental Controls, Document 30.1, Managing Environmental Aspects through Pollution Prevention*, UCRL-AM-133867-VOL-3-30.1-2009.

Martins, Stan (1996), *Building 5475 Soil-Vapor Extraction Treatment Test Results (LX-131)*, December, 1996.

Terranear PMC, (2008), *Environmental Restorations Department's Site Restoration Treatment Systems Assessment*, LLNL Livermore Site, Livermore California, July 2008.

Weiss Associates (2007), *Draft Authorized Limit Evaluation of Spent Granulated Activated Carbon Used for Vapor-Phase Remediation at the Lawrence Livermore National Laboratory, Livermore, California*, January 2007.

Figures

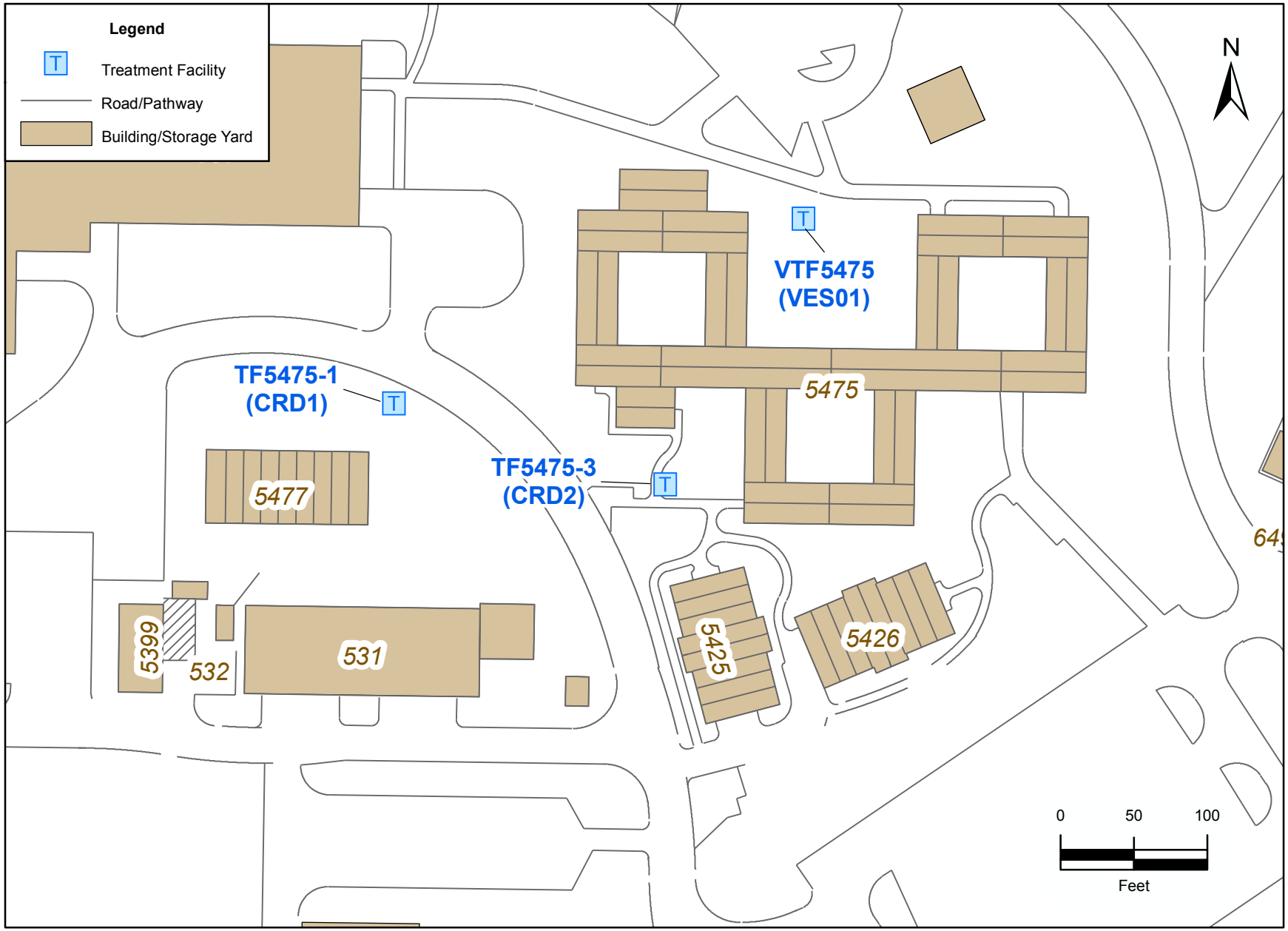

Figure 1. LLNL Livermore Site Trailer 5475 area and Treatment Facilities.

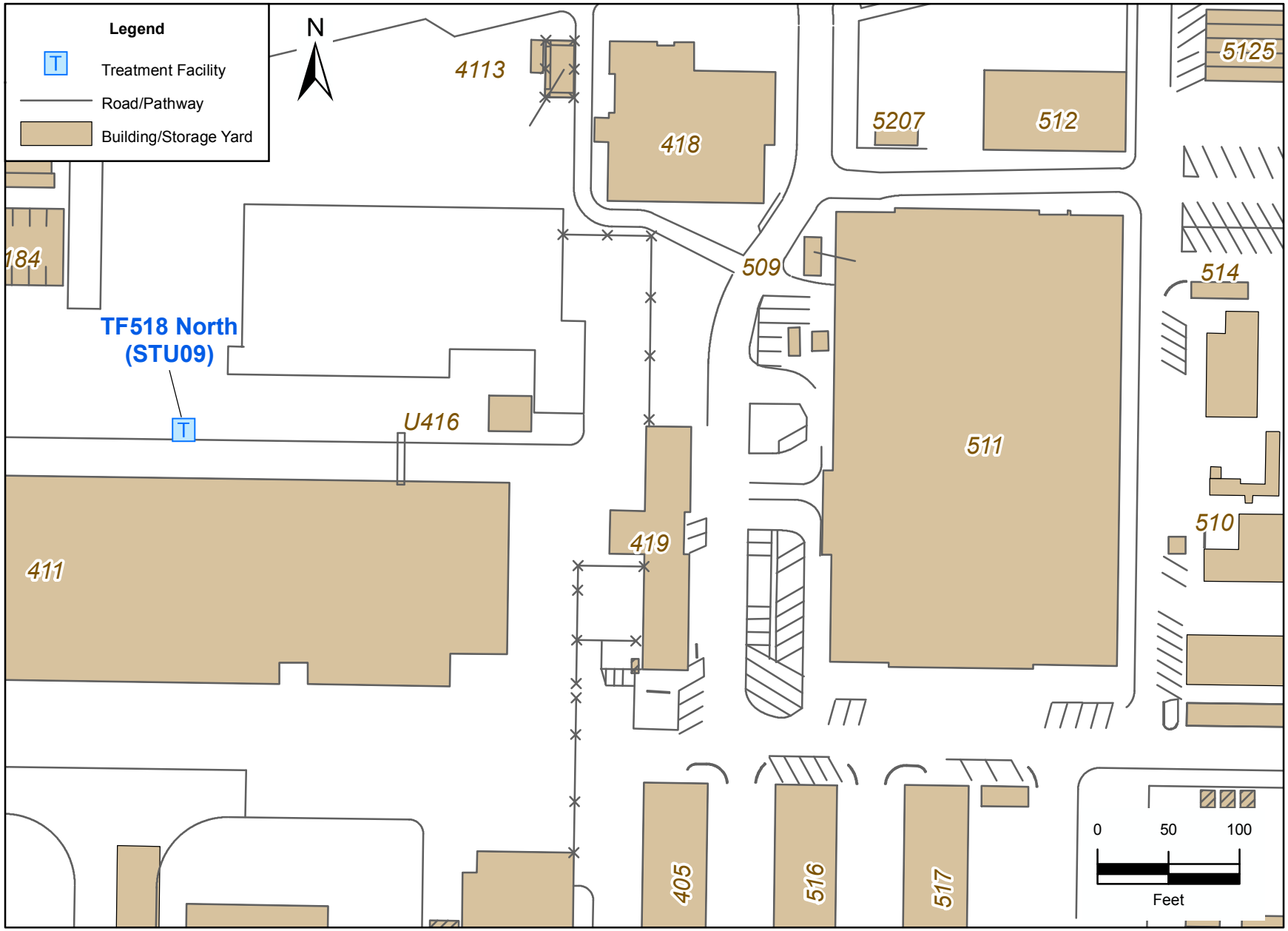

Figure 2. LLNL Livermore Site Treatment Facility 518 North and surrounding area.

LAWRENCE LIVERMORE NATIONAL LABORATORY

Lawrence Livermore National Security, LLC • Livermore, California • 94551